(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 577 420 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **93305165.8**

(51) Int. Cl.[5] : **H01M 8/12**

(22) Date of filing : **01.07.93**

(30) Priority : **01.07.92 US 907089**

(43) Date of publication of application :
05.01.94 Bulletin 94/01

(84) Designated Contracting States :
BE DE FR GB IT NL SE

(71) Applicant : **WESTINGHOUSE ELECTRIC CORPORATION**
Westinghouse Building Gateway Center
Pittsburgh Pennsylvania 15222 (US)

(72) Inventor : **Singh, Frabhakar**
2227 Woodmont Drive
Export, PA 15632 (US)
Inventor : **Ruka, Roswell John**
51 Churchill Road
Pittsburgh, PA 15235 (US)
Inventor : **Bratton, Raymond Joseph**
445 Manor Road
Delmont, PA 15626 (US)
Inventor : **Kuo, Lewis Jen-Hu**
3907 Stonecliffe Drive
Monroeville, PA 15146 (US)

(74) Representative : **van Berlyn, Ronald Gilbert**
23, Centre Heights
London NW3 6JG (GB)

(54) A fuel cell containing stable air electrode material.

(57) A tubular fuel cell (1) is made, containing a tubular, inner air electrode (3), a solid electrolyte (4), substantially surrounding the air electrode, and a porous outer fuel electrode (7), where the solid electrolyte and fuel electrode are discontinuous and have inclusion of an electrical interconnection material (6), where the air electrode (3) is a material selected from $La_xCa_yMnO_3$, where x has a value from .60 to .72 and y has a value from .28 to .40, or $La_xCa_yCr_zMn_{1-z}O_3$, where x has a value from .60 to .72, y has a value from .18 to .40, and z has a value from .05 to .15 and where a plurality of fuel cells can be electrically connected together.

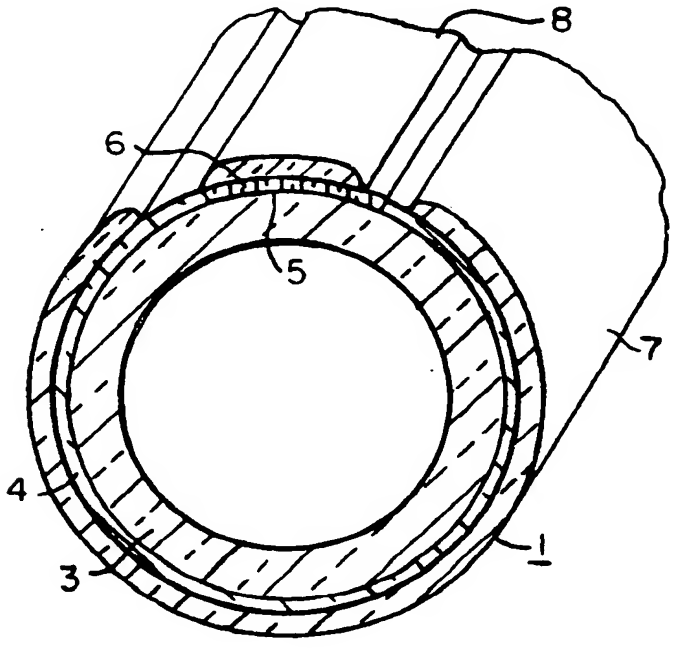

FIG.1

EP 0 577 420 A1

as 3. The cathode 3 is typically 1 millimeter to 3 millimeters thick and can be extruded or isostatically pressed to shape and then sintered. An optional stabilized zirconia support tube, not shown, can be used, if necessary, to support the air electrode. Over the air electrode is a gas-tight, dense, solid electrolyte 4, typically yttria stabilized zirconia, about 1 micrometer to about 100 micrometers thick.

A selected longitudinal segment 5 along the axial length of the cell is masked during deposition of the electrolyte and an interconnect material 6 is deposited on segment 5. The interconnect material 6 must be electronically conductive in both an oxygen and fuel environment. The interconnect is about 5 micrometers to about 100 micrometers thick and is typically made of dense lanthanum chromite doped with calcium, strontium, or magnesium. Surrounding the remainder of the cell except for the interconnect area is a fuel electrode 7 which functions as the anode. A typical anode is made of a metal ceramic (cermet) material and is about 30 micrometers to 100 micrometers thick. A coating material 8, which is of the same composition as the anode, can also be deposited over the interconnect 6. This material is typically nickel zirconia cermet and is about 50 micrometers to 100 micrometers thick.

In operation, a gaseous fuel, such as hydrogen or carbon monoxide, is directed over the outside of the cell, and a source of oxygen passes through the inside of the cell. The oxygen source forms oxygen ions at the air electrode-electrolyte interface, which migrate through the electrolyte material to the anode while electrons are collected at the cathode, thus generating a flow of electrical current in an external load circuit. A plurality of similar cells can be electrically connected by contact between the interconnect of one cell and the anode of another cell.

The porous air electrode remains exposed to the oxidant gas atmosphere, usually air, during generator operation, and oxygen reduction takes place at the air electrode-electrolyte interface. In the tubular cell configuration, the air electrode maintains intimate contact with the porous support tube when used, dense electrolyte, and dense interconnection film. Structural stability of the air electrode is an important requirement for maintaining long term mechanical integrity necessary for successful operation of the cell.

The cell length and the air electrode length usually range from 50 cm. to 230 cm. If air electrode length was 100 cm, the total heat shrinkage of even 0.05% in a 100 cm. length of porous air electrode in contact with dense electrolyte and interconnection would result in a 1/2 mm. difference in length between air electrode, electrolyte, and interconnection and would result in severe stresses between the materials. A marginal total heat shrinkage value would be from 0.03% to 0.04%, and long life commercially acceptable values are thought to be below about 0.02%. All components of the cell remain, under operating conditions, stable to shrinkage under isothermal conditions except the air electrode which has a tendency to shrink when subjected to certain thermal cycling conditions. This tendency to shrink translates into stresses between the air electrode and adjoining components and in some cases can result in cracking failure of individual cells, hampering operation of a multicell generator.

The air electrode 3 of this invention has a general formula consisting of $La_xCa_yCr_zMn_{1-z}O_3$, where x has a value from 0.60 to 0.72, y has a value from 0.28 to 0.40, and z has a value from 0 to 0.15. To this material, from 1 weight % to 12 weight % of ZrO_2 can be added when a calcia stabilized zirconia support tube is used, if necessary, to help bonding to the tube.

Thus, the air electrode can have the chemical formula: $La_{.60-.72}Ca_{.28-.40}MnO_3$ when Cr is not a component. The increased Ca doping makes the material less sensitive to accelerated shrinkage during cooling of the generator, which might occur during processing steps, operational malfunctions or special operational procedures.

Addition of Cr, however, in small amounts, helps to prevent oxygen loss at low oxygen pressures sometimes encountered during processing procedures, such as inter-connection or electrolyte deposition at 1200°C to 1400°C. Chromium when added is preferably within the range of z in the general formula of from .05 to 0.15. With Cr inclusion, the air electrode can have the chemical formula: $La_{.60-.72}Ca_{.18-.40}Cr_{.05-.15}Mn_{.85-.95}O_3$. Thus, the range of Ca can be lowered 10 atom % when Cr is added over 5 atom %. Inclusion of Cr for a value of z less than 0.05 will not appreciably enhance air electrode properties. The air electrode, to be useful in the fuel cell will be from about 20% porous to 40% porous (60% to 80% of theoretical density) preferably, from 20% porous to 35% porous (60% to 75% of theoretical density). The electrolyte and interconnection are both about 98% to 100% of theoretical density.

The following Examples further illustrate the invention and should not be considered limiting.

EXAMPLE 1

Sample test bars 2.54 cm. long, 0.635 cm. thick by 0.635 cm. wide were tested for dimensional stability during cycling from 25°C to 1000°C and holding for 4 hours, followed by dropping the temperature to 800°C and holding for 24 hours, followed by raising the temperature to 1000°C again and holding for 4 hours. Testing equipment was a Theta Industries, Dilatronic dilatometer. Individual dried oxide powders were mixed in exact

than 0.01% values of the Table I materials shows the dramatic advantage of the sample compositions of Table I.

Claims

1. A tubular fuel cell comprising a porous tubular inner air electrode, a gas tight solid electrolyte substantially surrounding the outer periphery of the air electrode, and a porous outer fuel electrode substantially surrounding the solid electrolyte, where the solid electrolyte and fuel electrode are discontinuous and have inclusion of an electrical interconnection material disposed on the air electrode in the discontinuity of the electrolyte, characterized in that the air electrode is a material selected from the group consisting of the composition $La_xCa_yMnO_3$, where x has a value from .60 to .72 and y has a value from .28 to .40, and the composition $La_xCa_yCr_zMn_{1-z}O_3$, where x has a value from .60 to .72, y has a value from .18 to .40 and z has a value from .05 to .15.

2. The fuel cell of claim 1, characterized in that the air electrode composition is $La_xCa_yMnO_3$, where x has a value from .60 to .72 and y has a value from .28 to .40.

3. The fuel cell of claim 1, characterized in that the air electrode composition is $La_xC_{ay}Cr_zMn_{1-z}O_3$, where x has a value from .60 to .72, y has a value from .18 to .40, and z has a value from .05 to .15.

4. The fuel cell of claim 1, characterized in that the air electrode is a self-supporting structure.

5. The fuel cell of claim 1, characterized in that the air electrode is from 20% porous to 40% porous.

6. The fuel cell of claim 1, characterized in that the air electrode is from 20% porous to 35% porous.

7. The fuel cell of claim 1, characterized in that the interconnect is dense and made of doped lanthanum chromite, the electrolyte is dense and made of stabilized zirconia, and the fuel electrode is made of nickel zirconia cermet.

8. The fuel cell of claim 1 electrically connected to a plurality of similar cells.

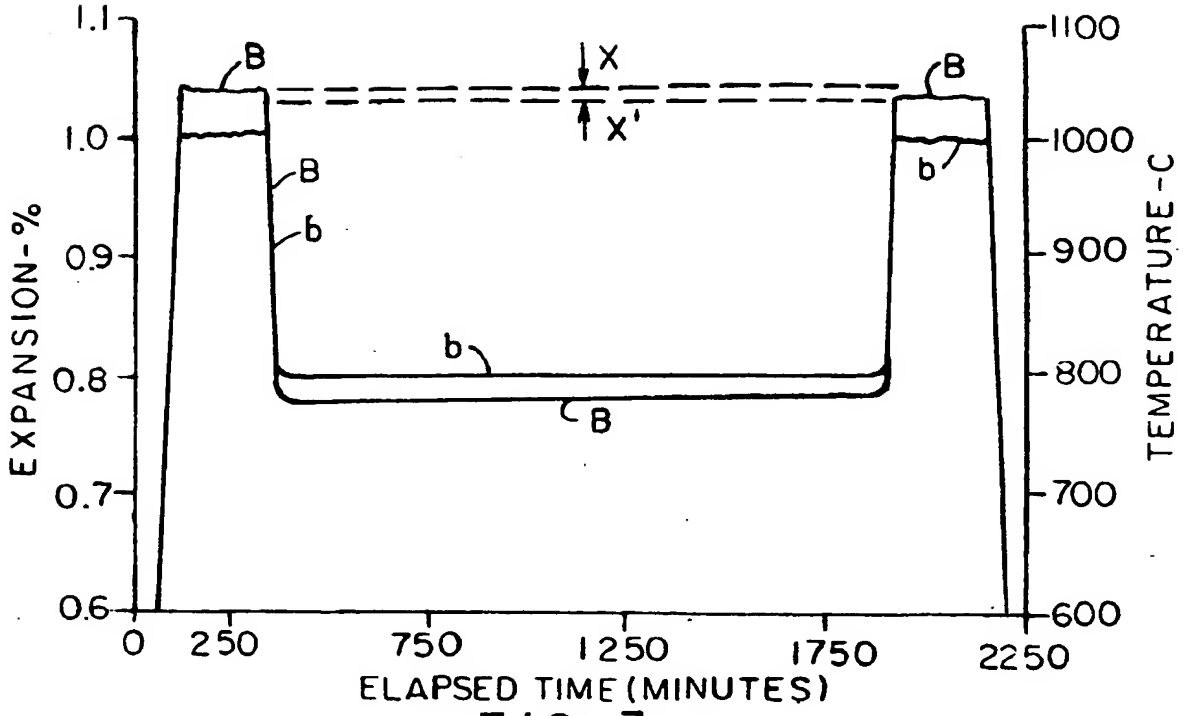
1.1
1.0
0.9
0.8
0.7
0.6
EXPANSION-%
1100
1000
900
800
700
600
TEMPERATURE-C
0
250
750
1250
1750
2250
ELAPSED TIME (MINUTES)
B
X
X'
b

FIG. 3

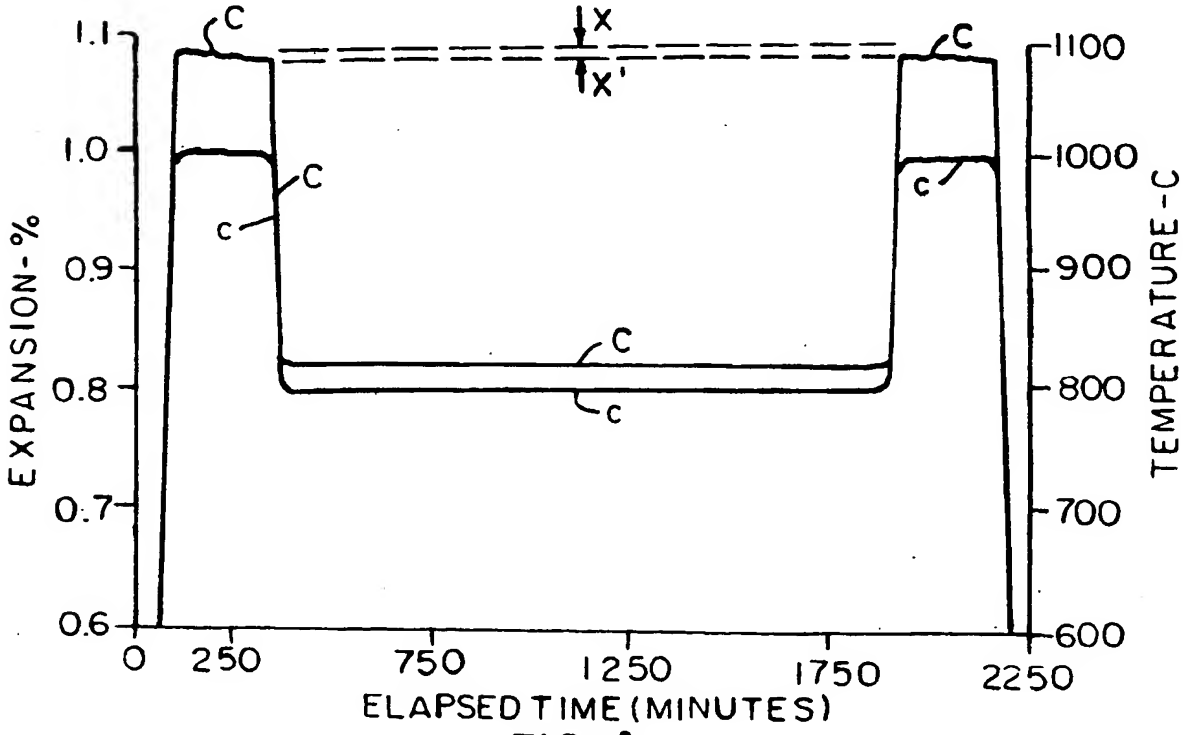
1.1
1.0
0.9
0.8
0.7
0.6
EXPANSION-%
1100
1000
900
800
700
600
TEMPERATURE-C
0
250
750
1250
1750
2250
ELAPSED TIME (MINUTES)
C
X
X'
c

FIG. 4

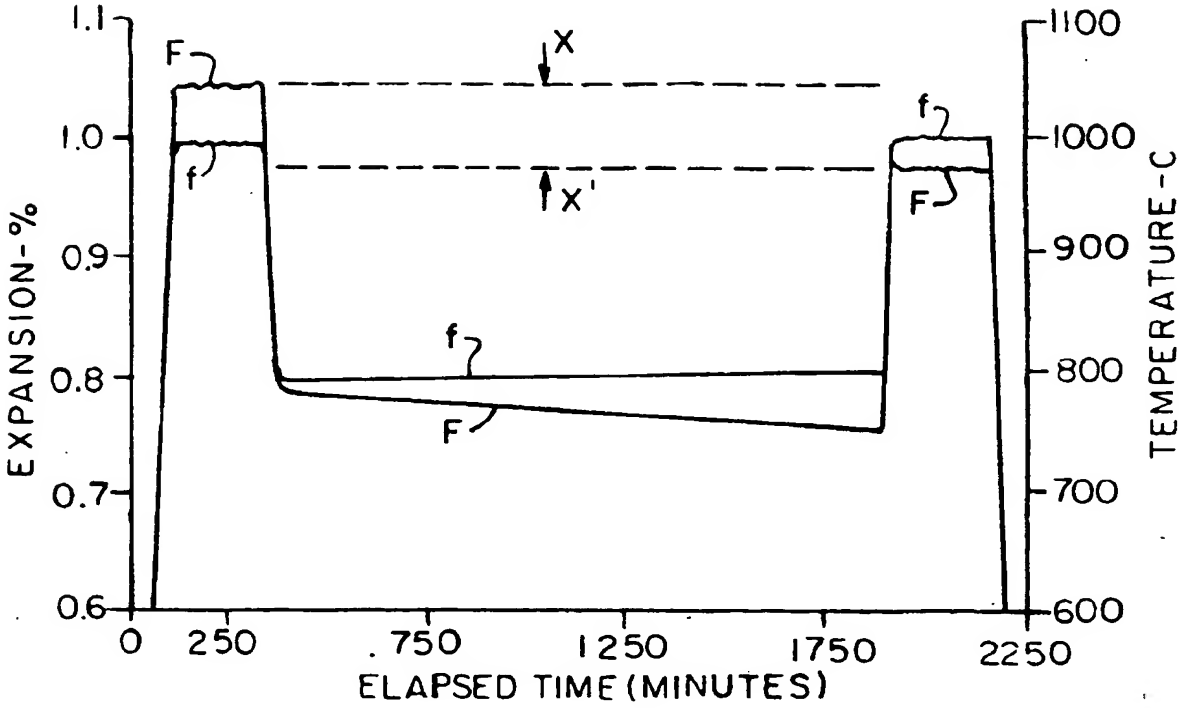
1.1
1.0
0.9
0.8
0.7
0.6
EXPANSION-%
1100
1000
900
800
700
600
TEMPERATURE-C
0
250
750
1250
1750
2250
ELAPSED TIME (MINUTES)
X
X'
F
f
f
F
f
F

FIG.7

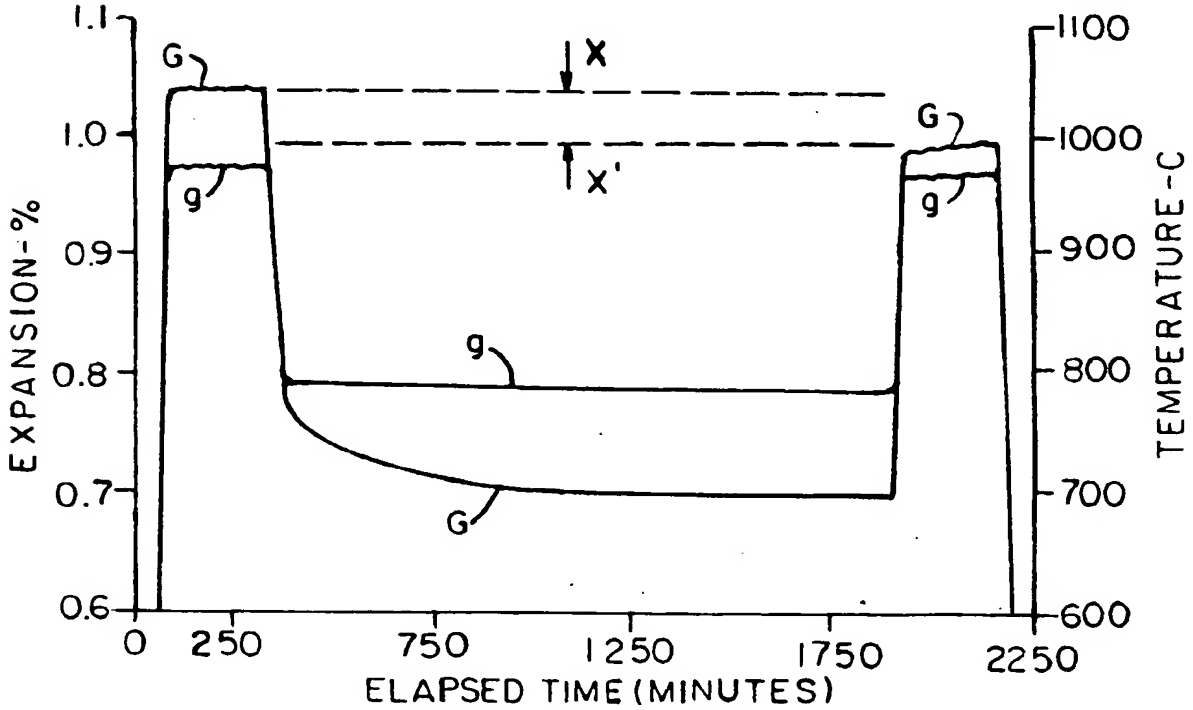
1.1
1.0
0.9
0.8
0.7
0.6
EXPANSION-%
1100
1000
900
800
700
600
TEMPERATURE-C
0
250
750
1250
1750
2250
ELAPSED TIME (MINUTES)
X
X'
G
g
g
G
g
G

FIG.8

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 5165

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JOURNAL OF THE ELECTROCHEMICAL SOCIETY vol. 138, no. 7, July 1991, MANCHESTER, NEW HAMPSHIRE US pages 1867 - 1873 JUNICHIRO MIZUSAKI ET AL 'Reaction Kinetics and Microstructure of the Solid Oxide Fuel Cells Air Electrode La0,6Ca0,4MnO3/YSZ' * abstract * * page 1868, left column, line 42 - line 50 *	1,2,5,6	
X	EP-A-0 467 590 (NGK INSULATORS) * page 2, line 11 - line 26; claim 1 * * page 2, line 36 - line 38 * * page 3, line 8 - line 12 *	1,2,4-6	
X	JP-A-01 200 560 (MITSUBISHI HEAVY IND LTD) * examples 8,9,10,12; table 1 * & PATENT ABSTRACTS OF JAPAN vol. 13, no. 496 (E-843)9 November 1989 * abstract *	1-3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 OCTOBER 1993	D'HONDT J.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0601)